

**(19) World Intellectual Property Organization
International Bureau**



(43) International Publication Date
30 May 2002 (30.05.2002)

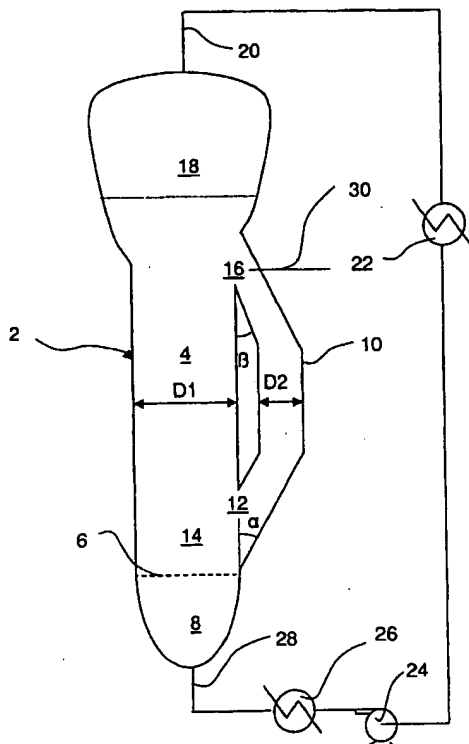
(10) International Publication Number
WO 02/41986 A1

PCT

- (51) **International Patent Classification?**: B01J 8/24, 8/38, C08F 10/00
- (21) **International Application Number:** PCT/NL01/00796
- (22) **International Filing Date:** 30 October 2001 (30.10.2001)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
1016681 22 November 2000 (22.11.2000) NL
- (71) **Applicant (for all designated States except US):** DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).
- (72) **Inventor; and**
- (75) **Inventor/Applicant (for US only):** MUTSERS, Stanislaus, Martinus, Petrus [NL/NL]; Eindstraat 9, NL-6166 EH Geleen (NL).
- (84) **Agent:** NIEUWKAMP, Johannes, Gerardus, Maria; DSM Patents & Trademarks, P.O. Box 9, NL-6160 MA Geleen (NL).
- (81) **Designated States (national):** AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) **Designated States (regional):** ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: FLUIDISED BED REACTOR



(57) Abstract: Fluidised bed reactor (1) which comprises a reaction chamber (4) which when in operation is in essence in vertical position, with a bottomsection which with a boundary plane connects with an inlet section (8) located below it and a top section which connects to an outlet section (18) located above it, which reactor (2) also comprises one or more connecting pipes (10) running outside the reactor chamber (4) and connecting the bottom part of the reactor chamber with the top section thereof and/or with the outlet section.

WO 02/41986 A1

WO 02/41986 A1



Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

FLUIDISED BED REACTOR

5 The invention relates to a fluidised bed reactor for the gas-phase polymerisation of one or more olefins, which comprises a reaction chamber which when in operation is in essence in vertical position, with a bottom section which with a boundary plane connects with an inlet section located below it and a top section which connects to an outlet section located above it.

10 The gas-phase polymerisation of olefins in a fluidised bed is effected in an elongated, normally vertically installed, reactor in which a bed of polymer particles is maintained in a fluidised state by means of a rising gas stream which contains at least the gaseous monomers to be polymerised. The gas supply is effected substantially via one or more inlets at the inlet section of the reactor, which inlets are located below the boundary plane. At the boundary plane
15 there may be a gas distribution plate that separates the reactor bottom section from the reaction chamber proper. Reactors of this type are disclosed in WO-A-94/28032 and in US-A-4,543,399. This plate then contains apertures which distribute the supplied gas stream across the area of the reaction zone as required. The boundary plane may also form an open connection, covering at
20 least 20% of its surface area, between the inlet section and the reaction chamber. A reactor of this type is disclosed in DE-19821955-A1.

 The rising gas stream may also contain one or more inert gases and for example hydrogen as a chain length regulator. An important objective of
25 the addition of inert gases is to control the gas mixture's dew-point. Suitable inert gases are for example inert hydrocarbons such as propane, (iso)butane, (iso)pentane and (iso)hexane, but also nitrogen. They may be added to the gas stream either as a gas or in a condensed form as a liquid.

 On exiting from the reaction chamber, the gas stream enters the
30 outlet section located above and is discharged through the top of the reactor. Viewed from the reaction chamber upwards, the outlet section usually widens so as to reduce the gas velocity and so prevent or minimise entrainment of the formed polymer particles with the gas stream leaving the reactor. Fresh monomer is added to the discharged gas stream, after certain treatments, to replace the
35 monomer consumed in the polymerisation, after which it is returned to the reactor as (part of) the rising gas stream to keep the bed fluidised. In addition, a catalyst is added to the bed. During the process, new polymer is constantly formed under

the influence of the catalyst present, and at the same time some of the polymer formed is withdrawn from the bed, with the bed volume being kept substantially constant. Converted monomer is continuously made up for, like via the gas stream that maintains the fluidised bed.

5 The polymerisation is an exothermic reaction. Heat must constantly be removed to maintain the temperature in the reactor at the required level. Such removal is effected via the gas stream, whose temperature when it leaves the reactor is higher than that at which it was supplied to the reactor. The gas velocity in the reactor cannot be chosen arbitrarily high, so it is not possible to
10 remove any desired amount of heat. The minimum local gas velocity is dictated by the requirement that the bed be kept in a fluidised state. On the other hand, the velocity must not be so high that the polymer particles are blown out through the top of the reactor. These limits are strongly determined by the dimensions and density of the polymer particles present in the bed and by the viscosity and
15 density of the gas stream, and can be determined by experiment. Practical values range from 10 to 100 cm/sec. At the given reactor dimensions, these requirements limit the maximum flow rate of the gas stream and, hence, the maximum attainable heat removal. As a consequence, the maximum permissible amount of heat of reaction produced, and thus the maximum amount of polymer to be
20 produced, are also limited.

 The detailed design and operation of fluidised bed reactors for polymerising olefinic monomers and suitable process conditions are known per se and are for example described in detail in WO-A-94/28032 and in US-A-4,543,399.

25 From this same US-A-4,543,399 it is known to add fresh monomer to make up for the gas stream discharged from the reactor and to cool the stream to such an extent as to cause it to partially condense. The two-phase stream obtained, which, owing to the latent heat of evaporation of the liquid part, has a substantially greater heat-removal capacity, and hence cooling capacity,
30 than a stream consisting exclusively of gas, is then supplied to the bottom of the reactor. The dew-point of the two-phase stream must be lower than the temperature in the reaction zone so that the liquid can evaporate in it. In this way, the production capacity of a fluidised bed reactor proves to increase substantially in comparison with the known reactors with otherwise the same dimensions.
35 According to the known method, the maximum amount of liquid in the two-phase stream is 20 wt.%. The highest figure quoted in the examples is 11.5%.

From WO-A-94/28032 it is also known to separate the liquid from the two-phase stream obtained on cooling the gas stream to be recycled and to supply the liquid to the reactor separately from the gas stream. The various embodiments and installations for supplying the liquid to the reactor as described therein may be applied in the reactor of the invention. This holds also for the dimensions, flow rates and ratios taught therein. It is preferred for the liquid to be injected or atomised into the fluidised bed at a particular elevation, optionally with the aid of a gaseous propellant. According to this publication, it is in this manner possible to supply a larger amount of liquid in relation to the amount of gas that is supplied. This allows even greater heat removal and so higher polymer production with correspondingly higher heat production. WO-A-94/28032 says that the maximum permissible ratio of the mass of liquid supplied to the mass of the total amount of gas supplied is 1.21, which figure is derived from a simulation experiment.

The present invention aims to provide a reactor which, with particular dimensions, allows a higher liquid/gas mass ratio of the feed to the reactor in gas-phase polymerisation of olefins in a fluidised bed reactor than in the known reactors.

This aim is achieved by the reactor also comprising one or more connecting pipes running outside the reactor chamber, which pipes connect the bottom part of the reactor chamber with the top part thereof and/or with the outlet section.

The presence of one or more connecting pipes has the surprising effect that more liquid, relative to the supplied amount of gas, can be supplied to the reactor than in the known reactors, while a stable fluidised bed being maintained. As a result, a higher production can be achieved than in the known reactors of equal dimensions.

An additional advantage of the reactor of the invention is that it is now possible to select a higher length/diameter ratio for the fluidised bed in the reactor, higher than for example 5 or even 10. This is much higher than is possible with the known reactors if a stable fluidised bed is to be maintained, affording better control of the polymerisation process. This advantage makes it possible to apply slimmer reactors, which presents substantial advantages in the design of polymerisation reactors, since these are pressure vessels.

A further advantage of the reactor of the invention is that the gas stream discharged via the top of the reactor contains a smaller amount of polymer

powder particles.

Yet another advantage of the reactor of the invention may be achieved when an inlet for adding fresh monomer is present at the connection of the connecting pipes to the wall of the top part of the reactor chamber or to the wall of the outlet section. "At" here means at a distance of not more than 3 x the square root of the cross-sectional area of the connecting opening of pipe and reactor chamber and not more than 1/3 times the diameter of the reaction chamber. Feeding fresh monomer at that particular position allows the gas composition in the connecting pipes to be varied and to differ from that in the reactor chamber. Hence, a product may be formed in the connecting pipes that has for example a different molecular weight or molecular weight distribution or, particularly in the manufacture of copolymers, a different chain structure.

The reactor of the invention distinguishes itself from the known reactors by the presence of one or more connecting pipes running outside the reactor chamber and connecting the bottom part of the reactor chamber with the top part thereof and/or with the outlet section.

The bottom part of the reaction chamber should be understood to mean that part thereof that connects at the boundary plane between the inlet section and the reaction chamber and extends to about 1 x the diameter D1 of the reaction chamber located above. The top part of the reaction chamber is that part which extends from the place where the reaction chamber connects to the outlet section to about 2 x D1 below.

The connecting pipes run outside the reaction chamber and preferably have a circular cross section although other shapes, for example that of a regular polygon, are also acceptable. The pipes have a central section which is substantially vertical (when the reactor is operated) and one or two connecting sections that are curved or folded towards the reactor to be able to be connected to the reactor wall.

The ratio of the total area of the largest cross sections perpendicular to the centre line of the connecting pipes to the area of the horizontal cross section of the reaction chamber is between 0.1 and 1.0, preferably between 0.1 and 0.3. In the case of a reaction chamber and a single connecting pipe with circular cross section, this corresponds with a diameter ratio D2 to D1 of the connecting pipe and the reaction chamber, respectively, of between about 0.3 and 1, preferably between about 0.3 and 0.55.

A connecting pipe preferably terminates in the wall of the

reaction chamber or of the outlet section and is preferably connected thereto at such angle that polymer build-up on the lower side of the wall of the connecting sections of the connecting pipe is prevented as much as possible. Thus, at both the bottom connection and the top connection of a connecting pipe to the reactor, the angle between the underside of the wall of the connecting section and the centre line of the reactor chamber is not more than 60° , preferably not more than 30° . The connecting pipes connect to a fitting connection opening in that wall. The opening to which the connecting pipe connects on the bottom part of the reaction chamber is located at least 50%, more preferably completely, in that bottom section and its lowest point may be located in the boundary plane or preferably up to $0.5 D_1$ above that plane. The low positioning of this opening has proved advantageous in achieving the aforementioned advantages of the reactor of the invention. The opening to which the top end of a connecting pipe connects to the reactor is preferably so positioned that the opening is fully immersed in the fluidised bed when the reactor is in operation. The said opening may be located completely in the wall of the reaction chamber but it has proved advantageous for the opening to be at least partly located in the wall of the widening section of the outlet section. It has been found that in that case the amount of polymer powder which is entrained by the gas stream via the top of the reactor is reduced still further. It is preferred for the opening to be located entirely in the wall of the widening outlet section. Since this wall is at an angle to the centre line of the reactor chamber, the upper connecting section of the connecting pipes may optionally be omitted or may be positioned at a smaller angle to the pipe than the bottom connecting section.

The cross section of the upper connecting opening preferably is smaller than or at the most equal to that of the bottom opening. It has been found that the connecting pipes then are less likely to become plugged. The ratio between the cross-sections of the top and bottom openings preferably is between 0.1 and 1, more preferably between 0.25 and 0.75. In order for this to be achieved, the upper connecting section of the connecting pipes may be tapered but the opening proper may also be reduced by mounting an adjustable valve or gate ahead of at least a portion thereof.

The connecting pipes may contact the outer wall of the reactor chamber but may also run at some distance therefrom, for example $0.5 \times D_1$. However, the aforementioned distance should preferably be as small as possible,

preferably smaller than $0.25 \times D1$. The connecting sections of the connecting pipes may then be kept short, which reduces the risk of polymer powder being left behind on the underside of the wall, which is not vertical.

The fluidising gas is supplied to the bottom of the reactor and
5 flows into the reactor chamber via the inlet section and through the boundary plane. It has proved advantageous for the gas supply not to homogeneously pass the boundary plane and reach the reaction chamber but such that more gas flows into the reaction chamber at points located further away from the connecting openings of the connecting pipes than nearer to those openings. For example, in
10 the case of only one connecting pipe being present, the average gas supply in one half of the boundary plane adjoining the wall section in which the connecting opening is present is smaller than in the other half of the boundary plane. If for example three connecting pipes are spaced along the circumference of the reactor at intervals of 120° , the gas supply in a central section of the boundary
15 plane - which section does not adjoin the reactor wall - whose area is equal to half the cross section of the boundary plane preferably is greater than that in the complementary peripheral section adjoining the wall throughout. Such asymmetric gas supply allows a further increase in the permissible amount of liquid. If a gas distribution plate is present in the boundary plane, the desired distribution of the
20 gas supply may be achieved by for example suitably selecting the number and/or size of the apertures therein. If no gas distribution plate is present, the inlet section may be asymmetric, with the gas being supplied substantially in those areas where the largest supply is desired. In that case use may also be made of objects and provisions present in the inlet section that distribute or direct the gas
25 stream. Suitable embodiments of such provisions for asymmetric supply of the gas stream to the bottom of a fluidised bed reactor are described in for example patent applications PCT/NL/000832 and PCT/NL/000834.

The liquid inlets may be located below or above the boundary plane. In the former case, the liquid may be mixed with the gases to be supplied
30 as it is passed to the inlet section but may also be passed separately thereto. In the latter case, the liquid may be supplied through inlets present in the wall of the inlet section or through inlets present in the wall of the reaction chamber. In the aforementioned latter case, if the supply is effected through the wall of the inlet section, the ends of the inlets should terminate above the boundary plane.

The reactor of the invention is suited in a process for preparing polyolefins in the gas phase by polymerising one or more olefinic monomers, at least one of which preferably is ethylene or propylene. Olefins preferably used in the process according to the invention are those containing 2 to 8 C atoms. Minor amounts of olefins containing more than 8 C atoms, for example containing 9 to 18 C atoms, may however also optionally be used. It is hence possible to prepare homopolymers of ethylene or propylene, copolymers of ethylene and propylene and copolymers of ethylene and/or propylene containing one or more $C_2 - C_8$ alpha-olefins in a preferred embodiment.

Preferred alpha-olefins are ethylene, propylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1 and octene-1. An example of a higher olefin that can be copolymerised with the primary ethylene or propylene monomer or that may partially replace the $C_2 - C_8$ monomer is decene-1. Dienes may also be used, for example 1,4-butadiene, 1,6-hexadiene, dicyclopentadiene, ethylidene norbornene, and vinyl norbornene.

Ziegler-Natta catalysts and other multiple-site catalysts may be used as catalyst in these processes, but so can single-site or multiple site catalysts, for example metallocene catalysts. The processes for the production of said polymers in a fluid-bed reactor that are known per se can be used in the reactor according to the invention, with the aforementioned advantages of the invention being achieved.

The reactor may be incorporated in known installations for gas-phase polymerisation. In that case, the reactor is provided at the top with an outlet for the unreacted reaction components. These reaction components then are passed through a pipeline to a compressor where they are compressed to the required inlet pressure so that they may be supplied to the reactor. In addition, the desired gas composition and gas flow rate are restored by supplying reacting components. As a rule, this process includes one or more cooling steps. In this way the reactor is operated in a continuous loop process. In order to allow the reactor to be operated in a so-called condensed mode, the compressed gases are cooled outside the reactor to the point where a proportion, in particular a proportion of the monomers and inert components, condense to form a liquid, whereupon this liquid is returned to the reactor either together with the components that have remained in the gaseous state or separately after being separated therefrom. Such reactor systems and processes for gas-phase manufacture of polymers are known per se, for example from the aforementioned

publications.

The invention therfor also relates to a process for polymerising one or more olefins in a gas-phase process in the reactor of the invention. In particular, in this process fresh monomer is supplied to the reactor at the topmost
5 connecting opening of the connecting pipes on the reactor. As previously explained, it is preferred for the fluidising gas to be supplied to the reactor in a form so that this gas is asymmetrically distributed over the boundary plane as it flows into the reaction chamber.

The invention is illustrated by means of the following figures.

10 Fig. 1 represents an axial cross section of a reactor of the invention with a bottom plate and one connecting pipe.

In Fig. 1, 2 is a cylindrical reactor in vertical position.

Reaction chamber 4 with diameter D_1 adjoins inlet section 8 at a gas distribution plate 6, which coincides with the boundary plane of reaction chamber 4. A
15 connecting pipe 10 with diameter D_2 equal to $0.4 \times D_1$ connects to an opening 12 in the bottom part 14 of reaction chamber 4. The angle between the connecting section of the connecting pipe and the centre line of the reaction chamber (in this case of a cylindrical reactor, the angle is equal to the one between the connecting section and the wall) is indicated by α and amounts to 30° . The lowest point of the
20 opening 12 is virtually at the same elevation as the top side of gas distribution plate 6.

The connecting pipe 10 connects at its top end to an opening 16 in the reactor wall. The opening is located partly in the wall of the reaction chamber and partly in the wall of the outlet section 18. The angle to the centre line
25 (in this case the angle to the wall) of the reaction chamber at which the connecting pipe 10 connects to the wall of the reaction chamber is indicated by β , which angle in this case is equal to 20° .

The rising gas stream is discharged through line 20 from the top of the reactor and is given a suitable temperature and pressure via a heat
30 exchanger 22, a pump 24 and a second heat exchanger 26 in order for it to be resupplied to the reactor as a gas-liquid mixture through supply line 28. It has proved advantageous when a feeding device 30 is present at opening 16 for feeding fresh monomer. The average height of the top of the fluidised bed under operating conditions is indicated by the dotted line 32. Not shown in the figure are
35 for example the catalyst feeder, the supply lines for make-up monomers and other

standard provisions that are present in condensed-mode gas-phase reactors. The assembly, make-up and functionality of these unshown means of processing and treating the discharged gas stream are known per se, in particular from the aforementioned publications WO-A-94/28032 and US-A-4,543,399.

CLAIMS

1. Fluidised bed reactor comprising a reaction chamber which when in operation is in essence in vertical position, with a bottom section which
5 with a boundary plane connects with an inlet section located below it and a top section which connects to an outlet section located above it, wherein the reactor also comprises one or more connecting pipes running outside the reactor chamber, which pipes connect the bottom part of the reactor chamber with the top part thereof and/or with the outlet section.
- 10 2. Fluidised bed reactor according to Claim 1, wherein the ratio of the total area of the largest cross sections perpendicular to the centre line of the connecting pipes to the area of a horizontal cross section of the reaction chamber is between 0.1 and 1.0.
- 15 3. Fluidised bed reactor according to Claim 1 or 2, wherein the bottom end of a connecting pipe terminates in the bottom section of the reaction chamber at a height of not more than 1 time the diameter of the reaction chamber.
- 20 4. Fluidised bed reactor according to any one of Claims 1-3, wherein the angle between the underside of a section of the connecting pipes that connects to the reactor wall and the centre line of the reactor chamber is not more than 60°.
5. Fluidised bed reactor according to any one of Claims 1-4, provided with means for asymmetric supply of fluidising gas to the reactor.
- 25 6. Process for polymerising one or more olefins in a gas-phase process, wherein the polymerisation is effected in a reactor according to any one of Claims 1-5.

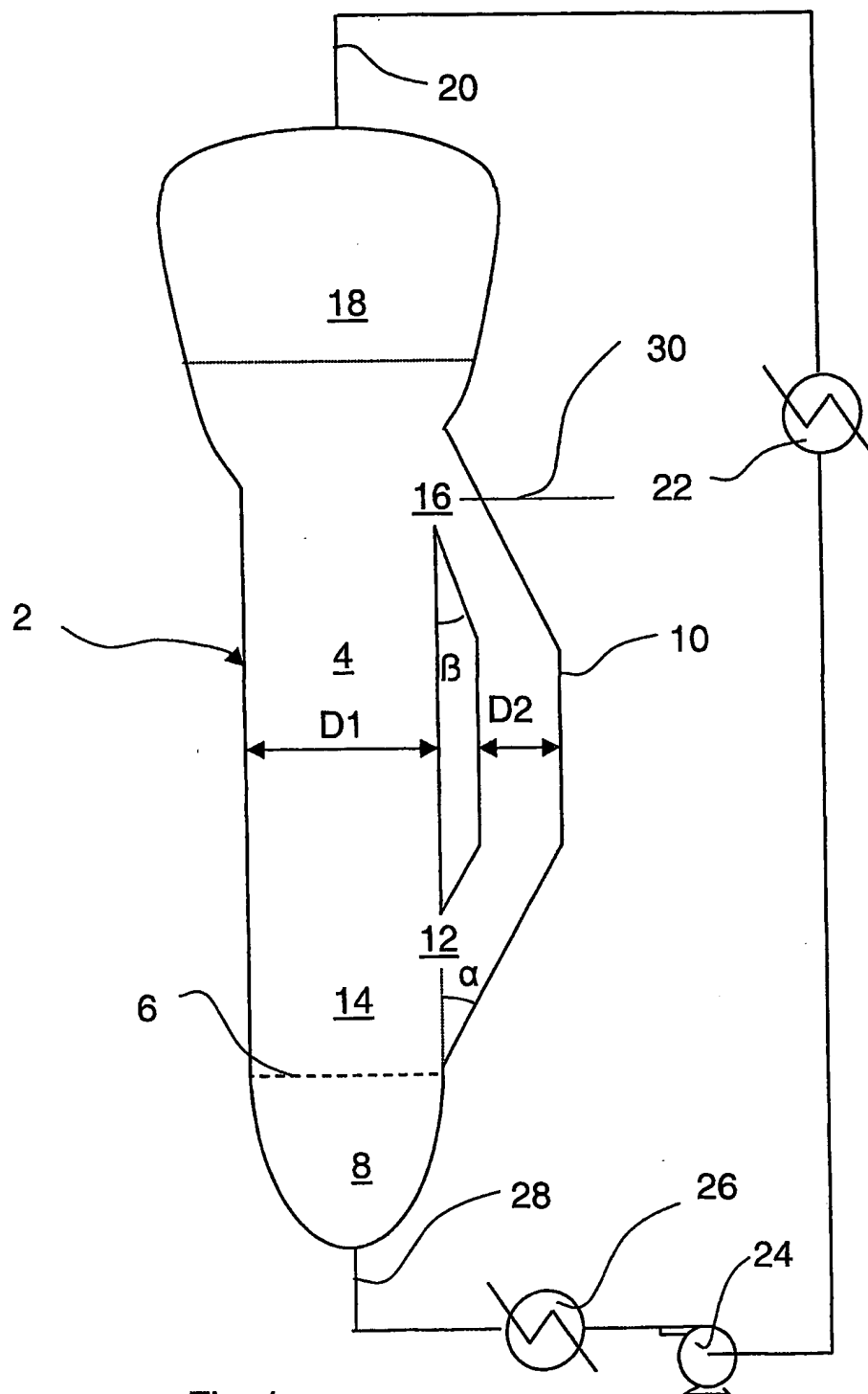


Fig. 1

INTERNATIONAL SEARCH REPORT

PCT/NL 01/00796

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 B01J8/24 B01J8/38 C08F10/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C08F F27B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 87 03668 A (AHLSTROEM OY) 18 June 1987 (1987-06-18) figure 1	1-4
X	US 4 932 363 A (KUIVALAINEN REIJO J) 12 June 1990 (1990-06-12) figures	1-4
X	AT 400 004 B (AUSTRIAN ENERGY & ENVIRONMENT SGP/WAAGNER-BIRO GMBH) 25 September 1995 (1995-09-25) figure	1,2
X	US 5 114 700 A (MEIHACK WOLFGANG F A T ET AL) 19 May 1992 (1992-05-19) figure 8	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

5 February 2002

Date of mailing of the international search report

13/02/2002

Name and mailing address of the ISA
 European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax (+31-70) 340-3016

Authorized officer

Van Belleghem, W

INTERNATIONAL SEARCH REPORT

PCT/NL 01/00796

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 8703668	A	18-06-1987	WO 8703668 A1	18-06-1987
			AT 58220 T	15-11-1990
			CA 1265660 A1	13-02-1990
			CN 86108105 A ,B	23-09-1987
			CN 1039736 A	21-02-1990
			CS 8609006 A3	18-11-1992
			DK 413087 A	07-08-1987
			EP 0311599 A1	19-04-1989
			FI 882623 A ,B,	03-06-1988
			KR 9101833 B1	26-03-1991
			US 4934281 A	19-06-1990
US 4932363	A	12-06-1990	FI 862069 A	20-11-1987
			AT 74415 T	15-04-1992
			BR 8707702 A	15-08-1989
			CN 87104041 A ,B	23-12-1987
			DE 3778020 D1	07-05-1992
			EP 0307406 A1	22-03-1989
			WO 8707356 A1	03-12-1987
			IN 169328 A1	28-09-1991
			JP 1039039 B	17-08-1989
			JP 1500612 T	01-03-1989
			KR 9101835 B1	26-03-1991
AT 400004	B	25-09-1995	AT 66994 A	15-01-1995
US 5114700	A	19-05-1992	AU 581103 B2	09-02-1989
			AU 6299886 A	26-03-1987
			CA 1277822 A1	18-12-1990
			ZA 8607101 A	27-05-1987